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KINETICS AND MECHANISM OF THE OXIDATION OF SOME HEXOSES BY SODIUM *N*-CHLOROBENZENESULPHONAMIDE IN THE PRESENCE OF SODIUM HYDROXIDE

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ABSTRACT

The kinetics of the oxidation of D-glucose, D-mannose, D-galactose and D-fructose by sodium *N*-chlorobenzenesulphonamide or Chloramine-B (CAB) in the presence of alkali at 35° has been investigated, and the rate = k[CAB][hexose][HO^-] was observed. The product, benzenesulphonamide, had no influence, increase of ionic strength increased the rate, and the rate decreased when the dielectric constant of the medium was decreased. The proton inventory was studied for the reactions in H_2O–D_2O mixtures. The rates increased in the order D-fructose > D-galactose > D-glucose > D-mannose. An isokinetic relation was observed with β 347 K, which showed the reaction to be enthalpy-controlled.

INTRODUCTION

Chloramine-T (p-$CH_3C_6H_4SO_2NClNa \cdot 3H_2O$, CAT) and Chloramine-B ($C_6H_5SO_2NClNa \cdot 1.5H_2O$, CAB) are used as disinfectants and antiseptics in preference to hypochlorites since they have greater stability. Both CAT and CAB have been extensively used as oxidants[1]. Their N–Cl bonds are highly polar and are sources of Cl^+.

Although CAB has been used widely as an oxidimetric reagent, little information is available on the kinetics and mechanism of these reactions. CAB is soluble in water, liberates iodine from acidified aqueous KI, and undergoes two-electron reactions to yield benzenesulphonamide and sodium chloride.

Although the kinetics of oxidation of aldoses by metal ions in acid solution have been reported[2], little information is available on their reactions with halogenating agents[3]. We now report on the kinetics of oxidation of D-glucose, D-mannose, D-galactose, and D-fructose by CAB in alkaline medium at 35°.

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EXPERIMENTAL

Chloramine-B was prepared by passing chlorine gas through a solution of benzenesulphonamide in 4M NaOH for 1 h at 70°. The product was collected, dried, and recrystallised from water. It had m.p. 170° with decomposition, and the purity was checked by iodometric titration and ^{1}H- and ^{13}C-n.m.r. spectroscopy.

An aqueous solution of CAB was standardised iodometrically and stored in brown bottles.

Triply distilled water was used in the preparation of aqueous solutions. The ionic strength of the reaction medium was kept at a constant high value by using conc. aqueous $NaClO_4$.

Regression analysis of experimental data was carried out with an EC-72 Statistical Calculator.

Kinetic measurements. — Reactions were carried out in glass-stoppered Pyrex boiling tubes in the dark in order to eliminate photochemical effects.

Requisite amounts of alkali, hexose, and $NaClO_4$ solutions and water (constant total volume) at 35° were treated rapidly with a solution of the oxidant also at 35°. The progress of each reaction was monitored by iodometric determination of unreacted CAB, and the reactions were followed for ~2 half-lives. The pseudo-first-order rate constants k_{obs} calculated from the log $[CAB]_0$ *vs.* time plots were reproducible to within ±3%. A slight deviation noted beyond 65% reaction may reflect the formation of acidic products. Hence, initial rates $(-dc/dt)_0$ were measured for various concentrations of oxidant, using the plane-mirror method[4] in the concentration–time plots. A plot of log $(-dc/dt)_0$ *vs.* log c had a slope of unity, confirming the first-order dependence of rate on $[CAB]_0$.

Stoichiometry. — Each reaction mixture containing substrate, NaOH, and excess of CAB was equilibrated for 48 h at 35°. The excess of oxidant was then determined iodometrically. The following stoichiometry was shown for D-glucose, D-mannose, and D-galactose;

$$C_nH_{2n}O_n + PhSO_2NClNa + H_2O \rightarrow C_nH_{2n}O_{n+1} + PhSO_2NH_2 + Na^+ + Cl^- \quad (1)$$

and for D-fructose.

$$C_6H_{12}O_6 + 2PhSO_2NCl\cdot Na + H_2O \rightarrow C_5H_{10}O_6 + HCOOH + 2PhSO_2NH_2 + Na^+ + Cl^- \quad (2)$$

Product analysis. — The benzenesulphonamide formed was extracted into ether and was then detected (R_F 0.88) by t.l.c. (2:2:1 light petroleum–chloroform–1-butanol) and detection with iodine.

After removal of the benzenesulphonamide, the residual solution was passed through columns of Amberlite IR-120 (H^+) and Dowex-2 (HO^-) resins in order to remove Na^+ and Cl^-, respectively. The final eluate was then concentrated to ~30%

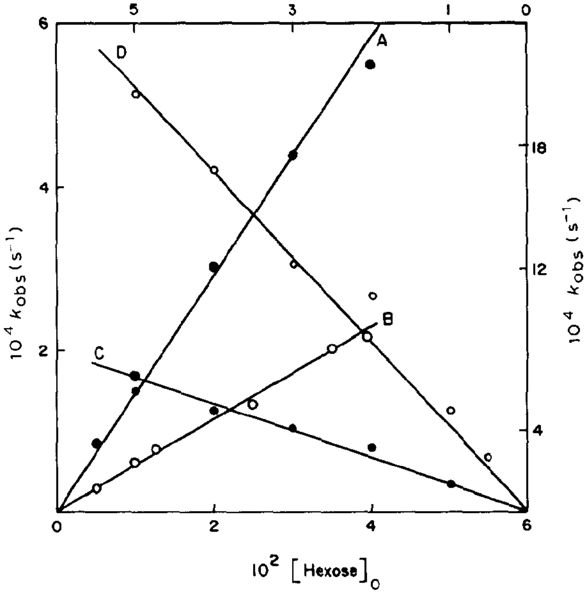


Fig. 1. Plots of k_{obs} *vs.* $[\text{Hexose}]_0$: A, D-glucose; B, D-mannose; C, D-galactose; D, D-fructose; $[\text{CAB}]_0 = 3 \times 10^{-3}$M, $[\text{HO}^-] = 0.1$M, I = 0.5M, temp. 35°.

and analysed by p.c. (1-butanol–acetic acid–water, 4:1:5) and detected with *p*-anisidine hydrochloride.

Formic acid was determined by the chromotropic acid procedure, after reducing it with magnesium powder in the presence of acid.

RESULTS

Reactant concentrations. — With the substrate in excess, at constant $[\text{HO}^-]$ and $[\text{hexose}]_0$, plots of log $[\text{CAB}]_0$ *vs.* time were linear, indicating a first-order dependence of rate on $[\text{CAB}]_0$ (Table I). Values of first-order rate constants, k_{obs}, increased with increase in $[\text{hexose}]_0$ (Table I). Plots of log k_{obs} *vs.* log $[\text{hexose}]_0$ were linear with almost unit slopes. Further, the second-order rate constant, $k_{obs}/[\text{hexose}]_0$, was a constant, confirming the first-order dependence of rate on $[\text{hexose}]_0$. A plot of k_{obs} *vs.* $[\text{hexose}]_0$ passes through the origin, indicating that the intermediate formed with oxidant is of transient existence (Fig. 1).

Concentration of alkali. — At constant $[\text{CAB}]_0$ and $[\text{hexose}]_0$, k_{obs} increased (Table II) with increase in [NaOH]. Plots of log k_{obs} *vs.* log [NaOH] were linear with unit slopes, thus illustrating the first-order dependence of rate on [alkali].

Effect of benzenesulphonamide and chloride ions. — Addition of the reaction product, benzenesulphonamide (BSA, 1.0–6.0 × 10^{-3}M), had a negligible effect on the rate, indicating that it was not involved in a pre-equilibrium with the oxidant. Addition of NaCl (4.0–10 × 10^{-3}M) to the reaction mixture had no effect on the rate, confirming the absence of free chlorine in the reaction sequence.

TABLE I

EFFECT OF REACTANT CONCENTRATIONS ON THE RATE OF OXIDATION OF HEXOSES AT 35°[a]

10^3 [CAB]$_o$ (M)	10^2 [Hexose]$_o$ (M)	10^4 k_{obs} (s^{-1})			
		D-Glucose	D-Mannose	D-Galactose	D-Fructose
1.0	2.0	2.97	1.24	3.32	11.27
2.0	2.0	2.97	1.25	3.21	11.23
3.0	2.0	3.03	1.25	3.21	10.61
4.0	2.0	2.99	1.26	3.17	10.61
4.5	2.0	3.03	1.25	3.18	10.45
5.0	2.0	3.04	1.20	3.24	10.61
5.5	2.0	3.04	1.23	3.20	10.07
6.0	2.0	2.97	1.20	3.09	10.45
3.0	0.5	0.85	0.32	—	2.68
3.0	1.0	1.66	0.57	1.45	5.00
3.0	1.5	2.34	0.75	2.04	7.08
3.0	2.5	3.72	1.29	3.31	11.22
3.0	3.0	4.38	1.50	4.11	12.23
3.0	3.5	5.01	1.96	4.47	15.14
3.0	4.0	5.48	2.06	4.97	16.82
3.0	5.0	6.27	2.51	6.03	20.52

[a] $[HO^-] = 0.1$M, I = 0.5M.

Ionic strength. — The addition of 0.1–1M $NaClO_4$ increased the rate of reaction. Plots of log k_{obs} *vs.* $I^{1/2}$, where I is the ionic strength, were linear with fractional slopes of ~0.6 (Fig. 2).

Solvent. — The composition of the solvent was varied by adding methanol up to 40%. The rate decreased with increase in the percentage of methanol. Further, a plot of log k_{obs} *vs.* 1/D, where D is the dielectric constant of the medium[5], was linear with a negative slope (Fig. 3).

Temperature. — The reaction was studied in the range 304–323 K and, from the Arrhenius plots of log k_{obs} *vs.* $1/T$, kinetic and thermodynamic parameters were computed (Table III). The entropy of activation was obtained from the relation[6]

TABLE II

EFFECT OF [NaOH] ON THE RATE OF REACTION AT 35°[a]

10^2 [NaOH] (M)	10^4 k_{obs} (s^{-1})			
	D-Glucose	D-Mannose	D-Galactose	D-Fructose
6.0	1.87	0.73	1.60	6.77
8.0	2.71	1.02	2.20	7.98
10.0	3.03	1.25	3.21	10.61
12.0	3.81	1.70	3.59	12.73
14.0	4.67	1.88	3.90	14.07
20.0	5.64	1.90	5.50	20.52

[a] $[CAB]_o = 3.0 \times 10^{-3}$M, $[Hexose]_o = 2.0 \times 10^{-2}$M, I = 0.5M.

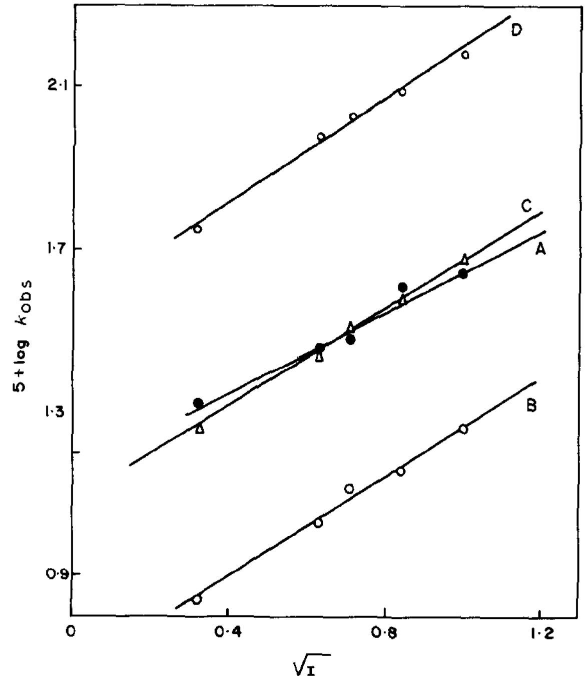


Fig. 2. Plots of log k_{obs} *vs.* $(I)^{1/2}$: $[CAB]_0 = 3 \times 10^{-3}$M, $[Hexose]_0 = 2 \times 10^{-2}$M, $[HO^-] = 0.1$M, temp. 35°.

$$\Delta S^\ddagger = \Delta H^\ddagger/T - 4.576 \log T/k_{obs} - 47.22,$$

where $\Delta H^\ddagger = E_a - RT$ is the enthalpy of activation at absolute temperature T, and k_{obs} is the rate constant in s^{-1}.

Isotope studies. — Solvent isotope studies were made using D_2O. For glucose, k_{obs} was $5.48 \times 10^{-4}s^{-1}$ in D_2O and $2.98 \times 10^{-4}s^{-1}$ in H_2O, leading to a solvent isotope effect, $k_{obs}(H_2O)/k_{obs}(D_2O)$, of 0.54.

Proton inventory studies with D-glucose as the probe were made in H_2O–D_2O mixtures, and the results are shown in Table IV. The corresponding proton inventory plot for the rate constant k^n_{obs} in a solvent mixture of deuterium atom fraction "n" is given in Fig. 4.

Test for free radicals. — Addition of acrylamide to the reaction mixture did not initiate polymerisation, showing the absence of free-radical species.

DISCUSSION

Although reports are available[7,8] on the equilibria present in solutions of CAT, no detailed information is available about the species present in solutions of

TABLE III

KINETIC AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF HEXOSES BY CAB IN PRESENCE OF SODIUM HYDROXIDE

Hexose	E_a *(kJ.mol^{-1})*	$\Delta H^\ddagger$ *(kJ.mol^{-1})*	$\Delta S^\ddagger$ *(J.K^{-1}.mol^{-1})*	$\Delta G^\ddagger$ *(kJ.mol^{-1})*	*Log A*
D-Glucose	101.2	98.6 ±0.1	+8.2 ±0.5	96.0 ±0.2	16.3 ±0.1
D-Mannose	113.7	111.1 ±0.1	+39.5 ±1.0	98.7 ±0.5	17.9 ±0.1
D-Galactose	99.5	96.8 ±0.1	+2.5 ±0.5	96.1 ±0.2	16.0 ±0.1
D-Fructose	69.0	66.4 ±0.1	−87.5 ±0.8	93.8 ±0.7	11.2 ±0.0

CAB. Zilberg[9] showed that the addition of HCl, H_2SO_4, or acetic acid to aqueous CAB produced Dichloramine-B ($PhSO_2NCl_2$) and benzenesulphonamide. Mogilevskii and co-workers[10] reported the presence of HOCl in acidified solutions of CAB. It is likely that equilibria similar to those of CAT exist in acidified solutions of CAB. The conductometric behaviour of solutions of CAB is identical[11] with that of CAT, and the pH titration curves observed were similar to those for CAT–HCl titrations[8,12]. Further, pH measurements on aqueous solutions of CAB showed that a 0.05M solution has a pH of 7.7 at 25°. Using these data, the ionisation constant K_a of $PhSO_2NHCl$ was found to be 2.4×10^{-3}, indicating it to be a stronger acid than the conjugate acid, $ArSO_2NHCl$ of Chloramine-T.

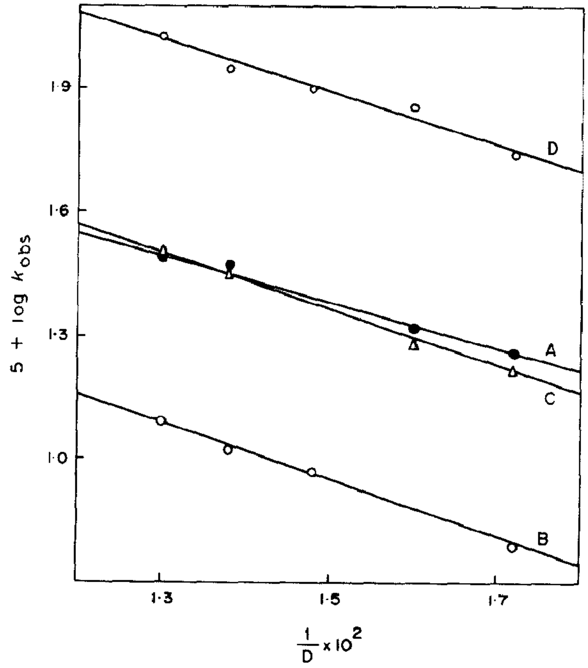


Fig. 3. Plots of log k_{obs} *vs.* 1/D: $[CAB]_o = 3 \times 10^{-3}$M, $[Hexose]_o = 2 \times 10^{-2}$M, $[HO^-] = 0.1$M, I = 0.5M, temp. 35°.

TABLE IV

PROTON INVENTORY PLOT FOR THE OXIDATION OF D-GLUCOSE BY CAB IN H_2O–D_2O MIXTURES AT 35°[a]

Atom fraction of deuterium (n)	*10^4k_{obs} (s^{-1})*
0.00	2.98
0.248	3.52
0.496	4.12
0.744	5.01
0.900	5.48

[a] $[CAB]_o = 3.0 \times 10^{-3}$M, $[Hexose]_o = 2.0 \times 10^{-2}$M, $[OH^-] = 0.1$M, I = 0.5M.

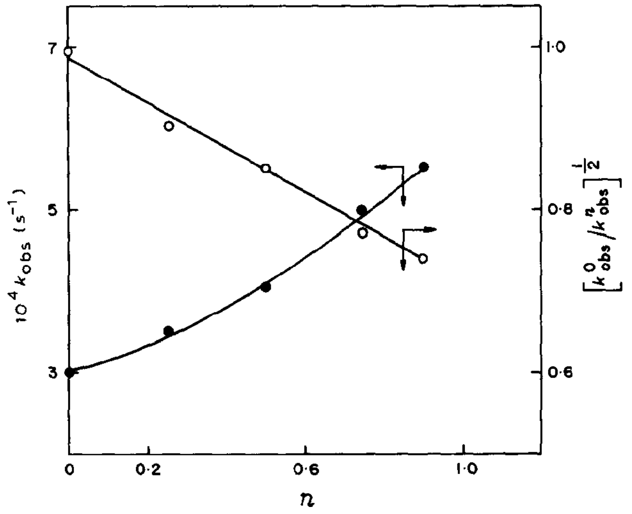


Fig. 4. Proton inventory plot for the oxidation of D-glucose by CAB in H_2O–D_2O mixture at 308 K. Experimental conditions as given in Table IV.

The following set of equilibria can be expected in acid CAB solutions.

$$PhSO_2NCl^- + H^+ \rightleftharpoons PhSO_2NHCl \qquad (3)$$
$$2PhSO_2NHCl \rightleftharpoons PhSO_2NH_2 + PhSO_2NCl_2 \qquad (4)$$
$$PhSO_2NCl_2 + H_2O \rightleftharpoons PhSO_2NHCl + HOCl \qquad (5)$$
$$PhSO_2NHCl + H_2O \rightleftharpoons PhSO_2NH_2 + HOCl \qquad (6)$$

The probable oxidising species in acidified solutions of CAB are $PhSO_2NHCl$, $PhSO_2NCl_2$, and HOCl.

In alkaline medium, the anion $PhSO_2NCl^-$ becomes important and the following equilibria are possible.

$$PhSO_2NCl^- + H_2O \rightleftharpoons PhSO_2NH_2 + OCl^- \qquad (7)$$

$$PhSO_2NCl^- + H_2O \rightleftharpoons PhSO_2NHCl + HO^- \qquad (8)$$

$$PhSO_2NHCl + H_2O \rightleftharpoons PhSO_2NH_2 + HOCl \qquad (9)$$

$$PhSO_2NHCl + HO^- \rightleftharpoons PhSO_2NH_2 + OCl^- \qquad (10)$$

The equations *7, 9* and *10* predict a retardation of rate by the reaction product, benzenesulphonamide (BSA), whereas equation *8* assumes a retardation of rate by HO^- ion. Since these are contrary to experimental observations, it is likely that the anion $PhSO_2NCl^-$ is the active oxidant species.

The experimental rate law is rate = k[CAB][S][HO^-], where S represents the hexose molecule, which occurs mostly as the β anomer. A tentative mechanism for explaining the first-order dependence of rate on the concentrations of oxidant, hexose, and HO^- and the nil effect of the reaction product, benzenesulphonamide, may be given by equations *11–13*.

$$S + PhSO_2NCl^- + HO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \qquad (11)$$

$$X \underset{\text{rate limiting}}{\overset{k_2}{\rightleftharpoons}} X^1 + RN^{2-} + HO^- \qquad (12)$$

$$X^1 \underset{\text{fast}}{\overset{k_3}{\longrightarrow}} \text{products} \qquad (13)$$

For D-fructose, equation *13* takes the form

$$X' + RNCl^- \longrightarrow \text{products} \qquad (14)$$

Assuming steady state conditions for the intermediate X, equation *15* can be derived for the disappearance of oxidant:

$$\text{Rate} = \frac{-d[CAB]}{dt} = \frac{k_2 k_1 [S][HO^-][CAB]}{k_{-1} + k_2} \qquad (15)$$

Proton inventory studies. — The increase of rate in D_2O supports the fast pre-equilibrium hydroxyl-ion transfer[13] (equation *11*). The dependence of rate constant (k^n_{obs}) on n, the atom fraction of deuterium, in a solvent mixture containing H_2O and D_2O is given[14,15] by equation *16*,

$$(k^{\text{o}}_{\text{obs}})/(k^{n}_{\text{obs}}) = \frac{\prod^{TS}(1 - n + n\phi_{\text{i}})}{\prod^{RS}(1 - n + n\phi_{\text{j}})}, \qquad (16)$$

where ϕ_{i} and ϕ_{j} are the isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition and reactant states, respectively. If it is assumed that the reaction proceeds through a single transition state, equation *16* can be transformed into equation *17*.

$$[(k^{\text{o}}_{\text{obs}})/(k^{n}_{\text{obs}})]^{1/2} = [1 + n(\phi_{\text{j}} - 1)] \qquad (17)$$

From the linear relation ($r = 0.9971$; $s = 0.04$) of equation *17* shown in Fig. 4, the slope ($\phi_{\text{j}} - 1) = (-0.27)$ from which $\phi_{\text{j}} = 0.72$. Kresge and Allred[16] obtained a value of 0.80 through n.m.r. studies for the isotopic fractionation factor of HO^-, and this was confirmed by Gold and Grist[17]. A similar value was noted in the kinetic studies of oxidation of aliphatic ketones by *N*-bromamines[18]. Considering the diversity of procedures employed, there is good agreement between the present and reported values for the fractionation factor of HO^-. Hence, the formation of a single transition state involving the participation of HO^- is supported.

Effect of ionic strength. — The rate increased with increase in the ionic strength (I) of medium. This finding is indicative of a primary salt effect and supports the involvement of two negative ions in the reaction sequence. Further, a plot of log k_{obs} *vs.* $(\text{I})^{1/2}$ was linear with a slope of ~0.6 (Fig. 2), although ionic strength was above the formal Debye–Huckel range.

Effect of the dielectric constant of medium. — The rate decreased with decrease in the dielectric constant (D) of the medium. A plot of log k_{obs} *vs.* 1/D was linear with a negative slope (Fig. 3). The effect of the composition of the solvent on rate for a reaction involving two negative ions is given by equation *18*, derived on the basis of the double-sphere model[19],

$$\log k = \log k_{\text{o}} - \frac{Z_{\text{A}}Z_{\text{B}}e^2}{\text{D}kT\,d_{\text{AB}}} \qquad (18)$$

where k_{o} is the rate constant in a medium of infinite dielectric constant, $Z_{\text{A}}e$ and $Z_{\text{B}}e$ are the charges, d_{AB} refers to the size of activated complex, and k and T are the Boltzmann constant and absolute temperature, respectively. From the slope = $-Z_{\text{A}}Z_{\text{B}}e^2/kT\,d_{\text{AB}}$, the size of activated complex (d_{AB}) was calculated to be between 3 and 5 Å: D-glucose (4.36 Å), D-galactose (3.50 Å), D-mannose (3.41 Å), and D-fructose (3.77 Å). The values are found to be reasonable in comparison with those of other reactions of similar nature[19].

Isokinetic relationship. — The data in Table III show that the energy of activation is highest for the slowest reaction, indicating that the reaction is enthalpy-

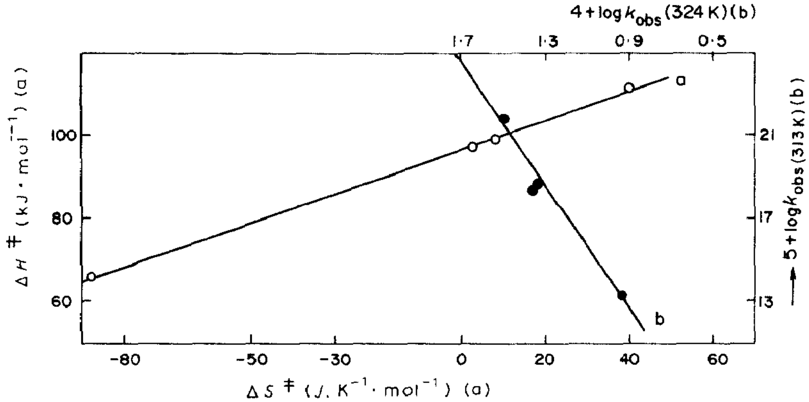
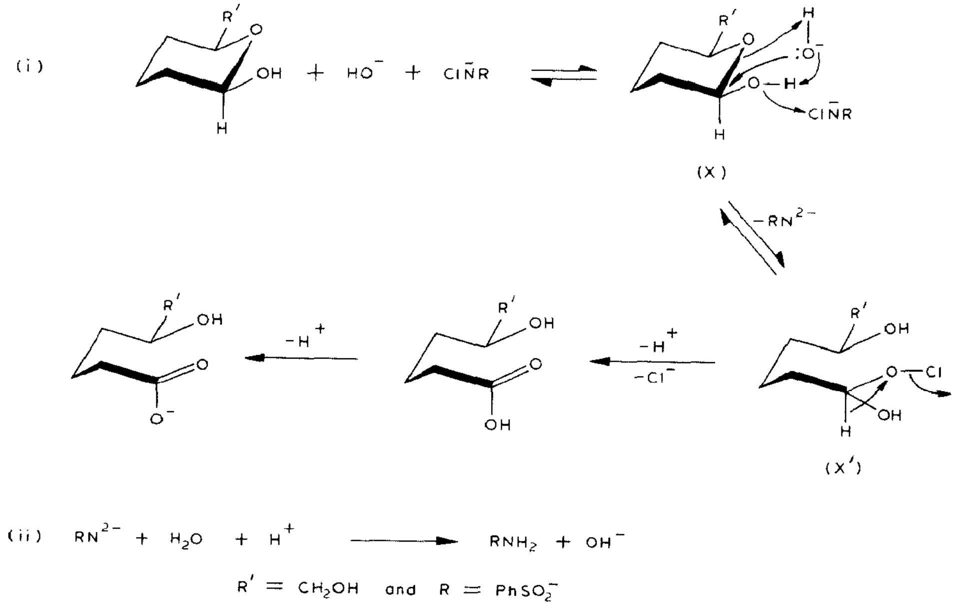


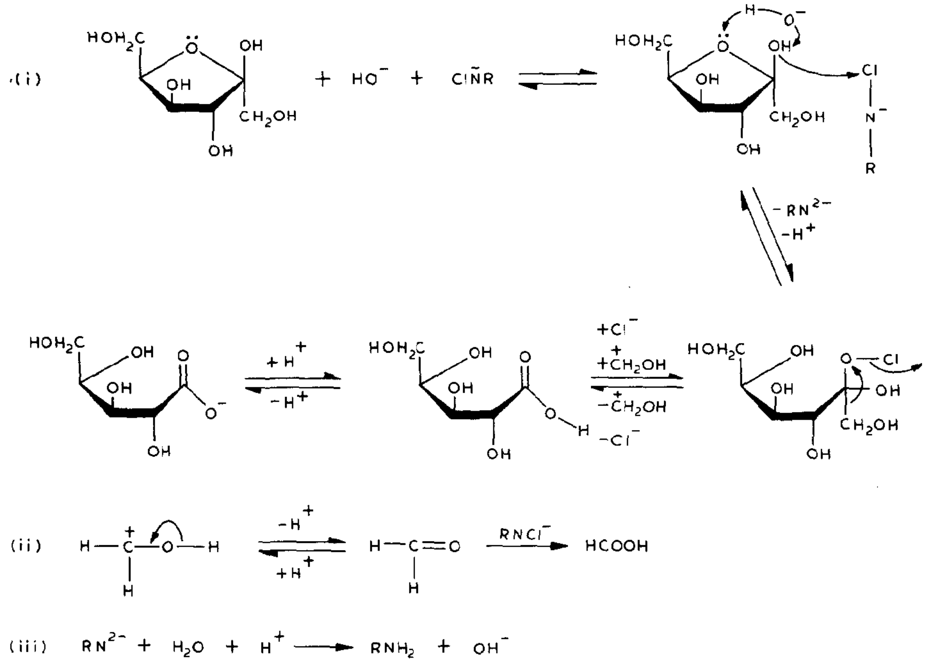
Fig. 5. Isokinetic plots of (a) $\Delta H^\ddagger$ *vs.* $\Delta S^\ddagger$ and (b) log k_{obs} (324 K) *vs.* log k_{obs} (313 K).

controlled. Further, values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ can be correlated linearly ($r = 0.9992$; $s = 0.04$), resulting in an isokinetic relation (Fig. 5), indicating that a common mechanism operates in the oxidation of hexoses by CAB. From the slope, the value of the isokinetic temperature β is 347 K, which is much higher than the experimental temperature. The relation was proved to be genuine through the Exner criterion[20] by plotting log k_{obs} (324 K) *vs.* log k_{obs} (313 K) ($r = 0.9922$; $s = 0.06$, Fig. 5). The value of β, calculated from the relation

$$\beta = T_l(1 - q)/\frac{T_1}{T_2} - q,$$



Scheme 1. A possible mechanism for the oxidation of D-glucose, D-mannose, and D-galactose by CAB in alkaline medium.



Scheme 2. Probable mechanism for the oxidation of D-fructose by CAB in alkaline medium.

where q is the slope of the Exner plot, was found to be 350 K, in agreement with the isokinetic point (347 K) calculated from the enthalpy–entropy relation.

A possible mode of oxidation of D-glucose, D-mannose, and D-galactose to the aldonic acids by CAB is shown in Scheme 1, and of D-fructose as in Scheme 2.

The aldohexoses exist in solution mainly as pyranoid forms, whereas D-fructose exists mainly in the furanoid form. The axial or equatorial orientation of HO-1 in the aldohexopyranoses will influence the rate of reaction. The form having HO-1 equatorial is more reactive due to the anomeric effect. The second-order rate constants ($10^2\ k''$; $L.mol^{-1}.s^{-1}$) follow the sequence, D-fructose, 5.31; D-galactose, 1.61; D-glucose, 1.52; and D-mannose, 0.63.

The rate is highest for D-fructose, which exists mainly in the furanose form, and slowest for D-mannose, for which the α-pyranose form with HO-1 axial is the major component[21] (~67%).

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